Special Report No. 1

DEVELOPMENT OF MATERIAL SPECIFICATIONS AND QUALIFICATIONS OF POLYMERIC MATERIALS FOR THE JPL SPACECRAFT MATERIALS GUIDEBOOK
1. EPOXIDE ADHESIVES

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950745
UNDER NASA CONTRACT NO. NAS7-100

JPL COGNIZANT ENGINEER: HUGH MAXWELL

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

*SRI

STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA

June 15, 1965

Special Report No. 1

DEVELOPMENT OF MATERIAL SPECIFICATIONS AND QUALIFICATIONS OF POLYMERIC MATERIALS FOR THE JPL SPACECRAFT MATERIALS GUIDEBOOK 1. EPOXIDE ADHESIVES

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950745
UNDER NASA CONTRACT NO. NAS7-100

JPL COGNIZANT ENGINEER: HUGH MAXWELL

By: JUDITH A. BLACK DONALD J. LYMAN DEAN B. PARKINSON

SRI Project PRD-5046

Approved: LIONEL A. DICKINSON, DIRECTOR
POLYMER AND PROPULSION SCIENCES DIVISION

Copy No. 149

CONTENTS

ILLUSTRATIONS

TABLES

SUMMARY

Nine Shell Epon* adhesives were selected by JPL cognizant engineer, Hugh Maxwell, for study under simulated space conditions. Outgassing characteristics of these materials were determined at 150° and 200°C at 10^{-6} mm Hg. Outgassed materials were analyzed by infrared and mass spectroscopy, and visual changes such as sample darkening and softening were noted. In thermal vacuum tests of these adhesives little change was observed at 150°C, but at 200°C there were large changes in the outgassing characteristics for most materials and in several cases unambiguous evidence of polymer degradation.

The following supporting experiments were performed. Tests of Epon 914 samples of varying thickness at 150°C showed that thickness of the test specimen had a profound effect on the outgassing characteristics. Epon 422J, an especially useful tape type adhesive, was subjected to various postcuring conditions before thermal vacuum treatment at 200°C; it was found that postcuring cycles of as little as six hours in air were sufficient to improve the outgassing characteristics to an acceptable level. The effects of purity of both the epoxy base and the amine curing agent on the outgassing characteristics of epoxy type adhesives were investigated by preparing "adhesive analogs" of the Epon systems using Bisphenol A and m-phenylene diamine as curing agent; the purity of the catalyst was found to be an important factor in determining the amount of weight lost in thermal vacuum treatments.

On the basis of these investigations, the Epons were classified for space use as: poor (Epon 934, 931, 924, and 914); borderline (Epon 941 and 903); and acceptable (Epon 917 and 901-B3). Epon 422J is acceptable only if postcured at 177°C.

*Trademark for Shell Chemical Company's epoxide adhesives.

INTRODUCTION

The over-all objective of this program is to provide assistance to the JPL staff members in the development of specifications and procedures for polymeric spacecraft materials. This includes definitions of properties, tests, and environments which are sensitive and meaningful, and collection of pertinent property, environmental, and materials data for use in specifications. Of particular importance to this program are the outgassing characteristics of various polymeric materials under thermal-vacuum conditions. The materials to be examined were selected by the JPL cognizant engineers.

The first class of materials selected for study were the general purpose structural adhesives of the epoxide type,[1] specifically the Epon adhesives. Samples were prepared and cured using recommended (by Shell and JPL) procedures and their weight loss characteristics were determined at 150°C and 10^{-6} mm Hg. This temperature (150°C) approximates the currently recommended sterilization temperature of spacecraft. In addition, the outgassed volatiles and condensables were analyzed to determine their source (i.e., additives, structural, abnormalities, chain degradation, etc.) so that improvements in the materials or in their processing conditions could be recommended.

Since most of these materials showed little change under these temperature conditions, data were also collected at 200°C. The results indicated the general stability of the polymeric material and thus provided insight into its structure-property relationship--knowledge which is important for guiding future spacefraft needs.

[1] JPL Spacecraft Materials Guidebook, Revision 3, 1964

EXPERIMENTAL

Materials

Epon adhesives 901-B3, 903, 914, 917, 924, 931AB, 934AB, 941, and 422J were obtained from Mr. Evan Blake, Adhesives Department, Plastic and Resins Division of the Shell Chemical Co., Pittsburg, California. These represent the purer fractions of standard production materials.

All samples were stored under refrigeration to minimize side reactions. This is particularly important with the 422J adhesive system because of high reactivity. The manufacturer recommends that the material be stored at temperatures below 0°C and a record kept of the time the adhesive is out of storage. The effect of warming seems to be cumulative and the 422J adhesive has a storage life of only 2 days at room temperature. A preliminary examination of the composition and purity of these adhesives was made using selected separation techniques and infrared spectroscopy. The data are summarized in Table I.

Preparation of Test Samples

Test samples of the resin were cast on specially prepared rectangular aluminum (Alclad 2024 T-3) strips, 2.7 cm wide and 11 cm long. Initially, 2-mil aluminum sheet was used, but later 11-mil aluminum sheet was found to be more satisfactory because the test samples did not curl during the thermal-vacuum treatments.

The aluminum strips were prepared for bonding by vapor degreasing with trichloroethylene and then etching with chromate solution (2:7:17 parts by weight $Na_2Cr_2O_7$: conc. H_2SO_4 : H_2O) at 66 ± 3°C for 10 minutes. The strips were rinsed thoroughly with distilled water and dried for 2 hours at 61°C.

Table I

SHELL EPON ADHESIVES

Adhesive No.	Description	Cured Epoxy Degradation Sample		
		Weight (g)	Area (cm^2)	Av. Thickness (mil)
901-B3	Two-part adhesive: (A) a gray thixotropic paste identified as Epon 828 with a metallic filler; (B) a dark-colored liquid curing agent identified[1] as an aromatic amine or amine mixture.	1.02582	22.0	15-20
903	A one-part adhesive in the form of a viscous gray paste. Identified[1] as based on Epon 828 and containing an unidentified catalyst and a mixed metallic-inorganic filler.	0.47728 0.39554	23.8 24.6	5
914	A one-part dark-gray thixotropic paste, reported stable indefinitely at room temperature. Identified[1] as based on Epon 828 with a dicyandiamide curing agent and metallic filler.	2.15919	23.1	30
917	A one-part adhesive based on an epoxy-anhydride system with a metallic filler. It is a free-flowing powder which melts at about 49°C (120°F) and does not resolidify on cooling.[2]	0.81566 1.09140	24.9 25.2	15
924	Pipe joint sealer and adhesive compound. Composition not identified.	0.44333 0.27743	24.8 24.3	5
931	A two-part adhesive: (A) a gray-black paste based on a novel epoxy system[1] other than the diglycidyl ether of Bisphenol A[3]; (B) a red liquid curing agent identified as an aromatic amine.	1.86748 1.89393	23.1 25.2	25
934	A room temperature curing two-part adhesive which meets the MIL-A-5090D, Type I requirements. Consists of a gray epoxy paste similar to that used in Epon 931[1] and an amber amine curing agent identified[1] as a polyamide. The filler is metallic.	1.4666 1.4767	23.1 24.3	15-20
941	Similar to 934, but has poorer quality control	0.87170 1.12772	24.2 24.6	15-20
422J	A gray tape-type adhesive meeting the MIL-A-5090D, Type III, class F requirements. A blend of epoxy and phenolic resins containing a metallic filler and dicyandiamide as curing agent. This blend is applied to 112-Volan A glass fabric support. The adhesive cures with evolution of volatiles to form a porous bond.	0.98980 0.96363	22.3 23.7	5

[1] Identification by infrared spectra and comparison with known sample

[2] The Epon 917 adhesive should not be accepted in any form but that of a free-flowing powder

[3] Epon 828 system is based on the diglycidyl ether of Bisphenol A.

A strip of masking tape was placed across the top of the aluminum strip during spreading of the adhesive; the tape was then peeled away to leave a resin-free area for ease in handling. Although the exact dimensions of the samples are not critical, the surface area to volume ratio should be within 5% of that given in the material specifications. The thickness of the test samples varies considerably for the various adhesive systems tested because of the widely differing viscosities of each system. (Note: The outgassing properties of these resins are highly sensitive to sample thickness.)

In the preparation of two-part adhesives, the need for adequate mixing of the two components cannot be overemphasized. Batches smaller than those recommended should not be prepared since larger weighing errors may be introduced, particularly in the curing agent, which could seriously affect the behavior of the adhesive. Mixing may be done manually using a spatula; Shell recommends vigorous stirring for at least 5 minutes, frequently scraping the spatula and the sides of the beaker. Detailed preparation of the test specimens is given below (letters refer to Table I, Description).

Epon 901-B3: The adhesive mixture was prepared by thoroughly mixing (vigorous stirring with a spatula) 11 g of Part B and 100 g of Part A. An even layer of the adhesive mixture, 15-20 mils thick, was applied to the etched aluminum strips using a camel's-hair brush. The samples were placed in a forced draft oven at 116°C (240°F) for 30 minutes; the temperature of the oven was then raised to 177°C (350°F) and the samples cured for an additional 90 minutes. The samples were pretreated for 55 hours at 24°C (77°F) and 3×10^{-6} mm Hg before use.

Epon 903: An even layer of adhesive, about 5 mils thick, was applied to the etched aluminum strips using a putty knife. The samples were cured for 2 hours in a forced draft oven at 177°C (350°F). The samples received no further treatment before thermal-vacuum testing.

Epon 914: An even layer of adhesive, approximately 30 mils thick, was applied to the etched aluminum strips with a putty knife. The samples were cured in a forced draft oven at 204°C (400°F) for 35 minutes. The samples received no further treatment before thermal-vacuum testing.

Epon 917: A thin, even layer of the powder was applied to one side of the etched aluminum strip with a camel's-hair brush and the sample warmed in an oven to hold it in place. The resulting layer of adhesive was approximately 15 mils thick. The adhesive was then cured for 60 minutes in a forced draft oven at 149°C (300°F). The samples received no further treatment before exposure to thermal-vacuum conditions.

Epon 931: The adhesive mixture was prepared by thoroughly mixing 9 g of Part B and 100 g of Part A with a spatula. The mixture was then spread on the etched aluminum strips with a putty knife to give a smooth, even layer approximately 25 mils thick. The samples were then cured in a forced draft oven at 161°C (250°F) for 60 minutes. The samples received no further treatment before thermal-vacuum testing.

Epon 934: The adhesive mixture was prepared by thoroughly mixing 33 g of Part B to 100 g of Part A with a spatula. The mixture was then spread on etched aluminum coupons using a putty knife, to give an even layer, 15-20 mils thick. The samples were cured at ambient temperature (20-25°C) for seven days. The samples received no further treatment before thermal-vacuum testing.

Epon 422J: The Epon 422J adhesive film was cut to the desired size, the polyethylene protective sheet removed from one side of the sample, and the exposed side placed on an etched aluminum strip. The remaining polyethylene protective sheet was then removed, and the exposed surface covered with a sheet of Teflon, then a pane of glass. Gentle pressure was applied to the samples to prevent air bubbles from forming during the curing. A schematic of this assembly is shown in Fig. 1. The samples were then cured in a forced draft oven at 166°C (300°F) for 30 minutes.

Epon adhesives 924 and 941 were prepared according to the Shell Epon Manual. Since these materials were not studied further, their descriptions are not included.

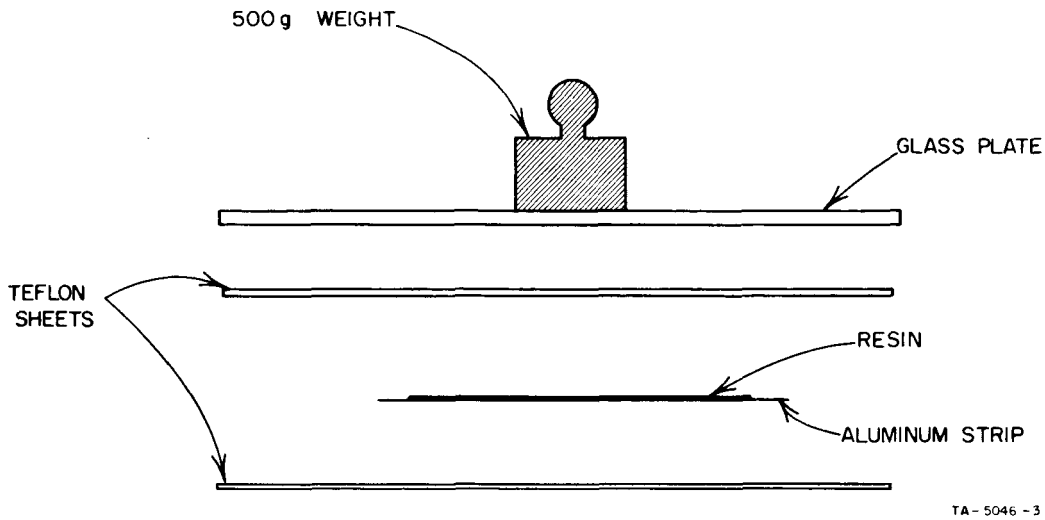


FIG. 1 SCHEMATIC DIAGRAM OF EPON 422J CURING ASSEMBLY

Equipment

The vacuum system (Fig. 2), which utilizes a mechanical roughing pump (capacity 140 liters per minute) and a mercury diffusion pump, can achieve routine pressures of 1-3 x 10^{-6} mm Hg. Pressures were measured with a Pirani ion gauge (Consolidated Vacuum Corp.) calibrated for pressures of .025 to 10^{-7} mm Hg. The adhesive test samples were placed in modified resin kettles (Fig. 3) which were heated by oil baths. The oil baths consisted of stainless steel beakers filled with Dow silicone oil No. 550 and heated by resin kettle heating mantles. The bath temperatures were controlled by Thermistemp temperature controllers (Yellowspring Instrument Co., Model 63RA), and the power to the heating mantles was supplied by a variable transformer. This arrangement maintained the oil baths at $\pm 2^{\circ}$ of the desired temperature. In general the bath temperatures were held about five degrees higher to maintain the desired sample temperature. The temperature of the oil baths was measured directly by a mercury thermometer suspended in the bath; the temperature inside the resin pot was determined from a thermocouple wire inserted into the thermocouple tube which extended into the resin pot. Temperature measurements were made using a Leeds and Northrup temperature potentiometer which read directly in degrees centigrade. (Measurements were accurate to approximately $\pm 0.5^{\circ}$ C.) The resin pot led directly to a

conventional trap cooled with liquid nitrogen which could be isolated from the rest of the system so that its contents could be transferred into a glass sample bulb suitable for analysis, such as infrared, mass spectrometry, etc.

The coated aluminum specimens were removed from the system for weighing to determine weight loss; weights were determined on a Mettler "H" balance, accurate to ±0.05 mg. Although continuous weighing under vacuum is recognized as a superior method, the present system will accommodate four different samples at one time and permits the rapid screening of materials as requested by JPL in this project.

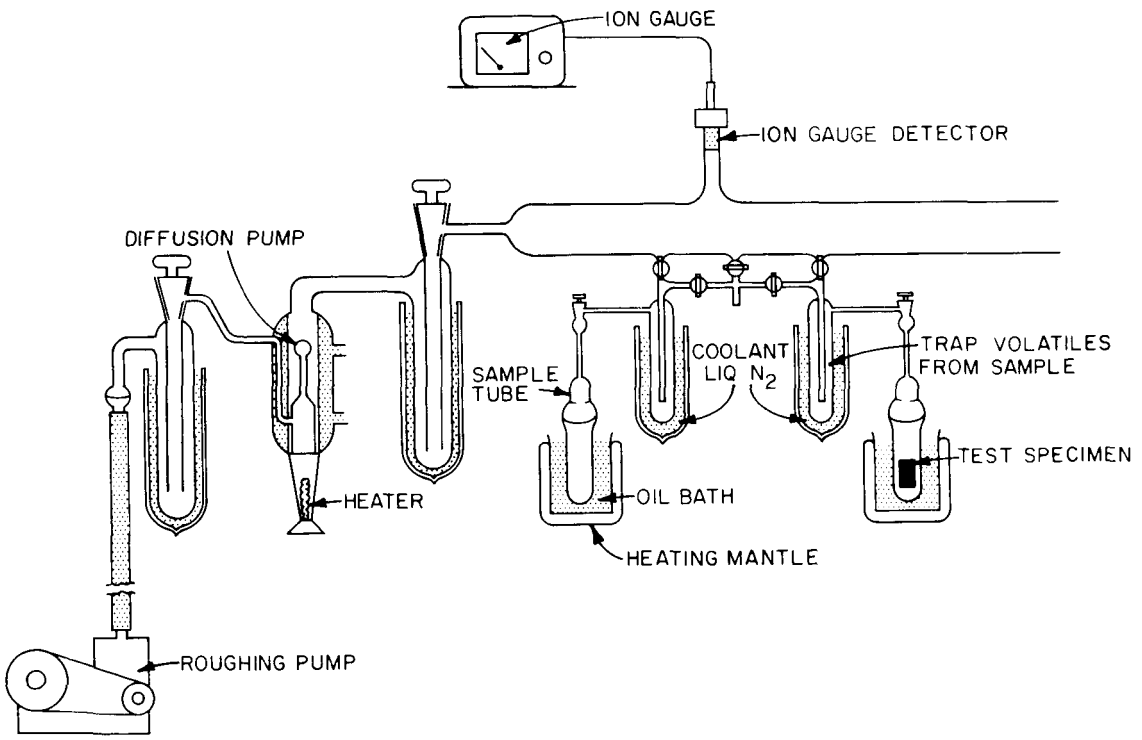


FIG. 2 COMPLETE VACUUM APPARATUS FOR THERMAL-VACUUM TREATMENT

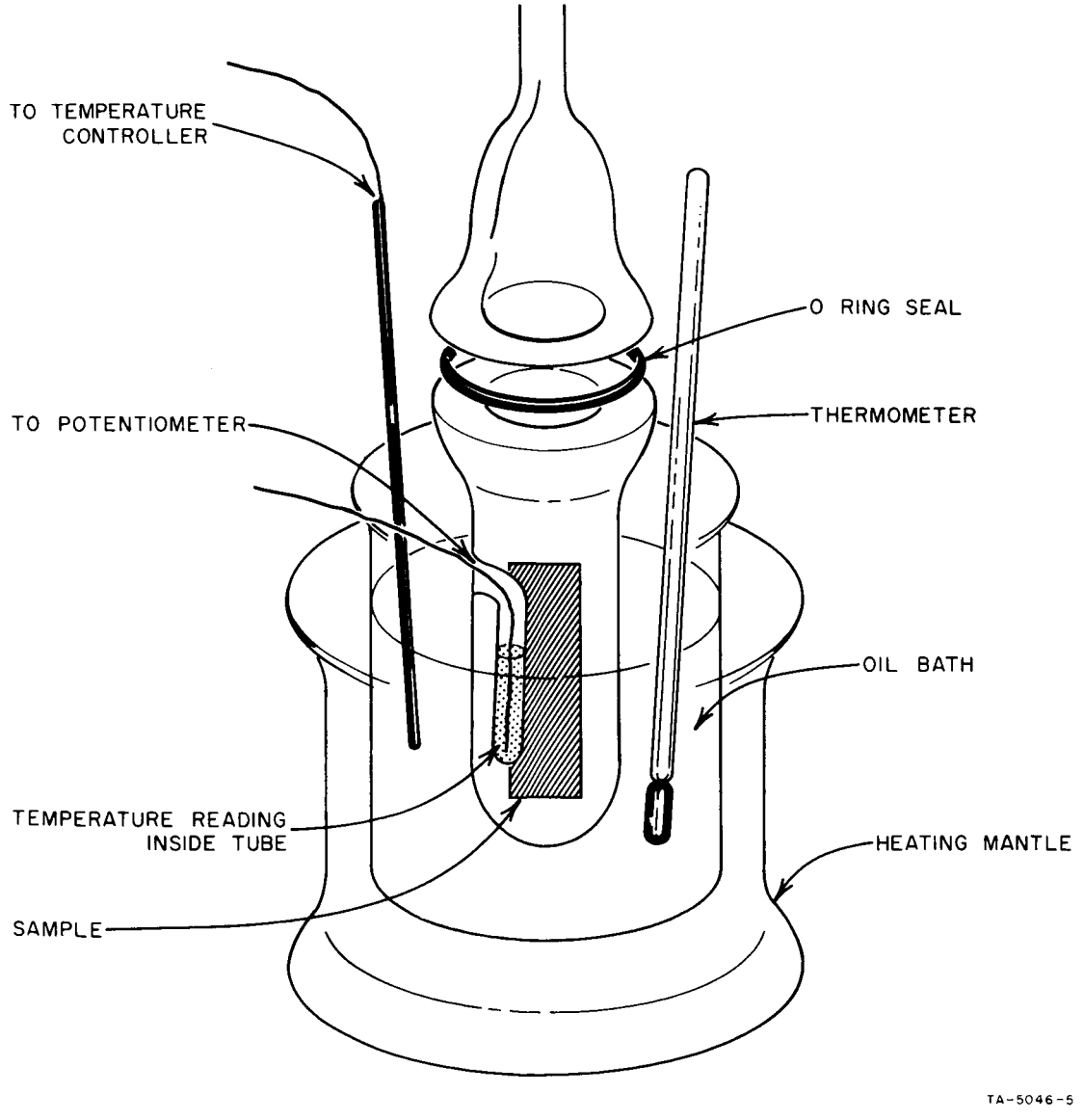


FIG. 3 DETAILED DRAWING OF SAMPLE CELL ASSEMBLY

Characterization of Polymeric Materials

The Epon adhesive samples were exposed to thermal-vacuum conditions in order to determine: (1) their weight loss; and (2) the nature of the outgassed material. In several instances, the effects of processing and postcuring conditions, and of polymer and catalyst purity on the outgassing characteristic of the epoxide adhesive were determined. The experimental techniques are described below.

Thermal Vacuum Testing Procedure

The cured Epon adhesive samples were tested at 150°C and 200°C and approximately 3×10^{-6} mm Hg for a total exposure of 150-200 hours. At approximately 24-hour intervals, the samples were removed for weighing. The temperature of the oil bath and the interior of the resin pot, and the pressure of the system were recorded at this time. The samples were removed from the traps with forceps and allowed to cool, then weighed to the nearest 0.01 mg and returned to the resin pots, which were immediately re-evacuated and the testing continued.

Samples for mass spectroscopic analysis were obtained at the conclusion of each thermal-vacuum test by vacuum-transfer of the material in the trap to a mass spectrometer sampler bulb. The bulb was evacuated, moisture removed by flaming, and the transfer accomplished by cooling the evacuated bulb in liquid nitrogen while the trap was warmed to room temperature (the trap-bulb system was isolated from the rest of the system during the transfer). Sample bulbs were stored in dry ice until a mass spectroscopic analysis could be performed.

The following raw data were recorded for each test: (1) weight and dimensions of cured samples; (2) weight of the sample to the nearest 0.01 mg at 24-hour intervals; (3) the temperature of the system; (4) any changes in color or other physical properties of the sample (5) observations relating to outgassed materials, such as condensable oils on the inside of the head of the resin pot, above the level of heating; (Note: If enough of the oil was evolved, an IR spectrum of the material was recorded) and (6) identification of any volatile material collected in

the cold traps by means of mass spectrometric analysis and infrared spectrometry. These data are tabulated in Tables II, III, IV, and V.

Infrared spectra were obtained using a Perkins-Elmer 221 Infrared Spectrophotometer. Mass spectroscopic analyses were obtained using a Consolidated Electrodynamics Corporation Model 21-103C.

Effect of Sample Thickness of Weight Losses

Epon 914 was selected for use in determining thickness effects on outgassing characteristics because of its good performance at 150°C. Samples of various thicknesses were prepared and cured as described previously. The absolute thickness of the material was calculated from the experimentally measured density of cured Epon 914 (2.44 g/cm^3). The effect of thickness on weight loss and weight loss rate were determined at 150°C and 10^{-6} mm Hg for a total exposure of up to 190 hours. Sample weight losses were measured at approximately 24-hour intervals. The data are shown in Table VI.

Effect of Material Purity on Weight Losses

The diglycidyl ether of "Bisphenol A" was selected as an experimental resin base since it was available commercially in both pure and commercial grade (impure) forms. The "impure" or commercial grade material, Epon 828, is a clear, low viscosity liquid; the "pure" grade Epon X-22 lot 1-62 is a white crystalline powder. m-Phenylene diamine, selected as a typical aromatic amine curing agent, was also obtained in an impure or commercial grade form, m.p. 62-64°C (Matheson, Coleman and Bell), and in a pure form by sublimation at 60°C/0.1 mm Hg. The sublimed material was a pure white crystalline solid which was stored under nitrogen atmosphere until use. Test specimens for thermal-vacuum testing were prepared by mixing 0.54 g of the amine curing agent with 10.0 g of the resin base; and all four possible combinations, i.e., pure resin and pure amine, pure resin and impure amine, impure resin and pure amine, and impure resin and impure amine were prepared. Because of the poor wetting properties of these unfilled adhesive mixtures, they were cast into aluminum foil cups about 3 cm in diameter and about 0.15 cm deep, rather than on the etched aluminum strips. The cups were lubricated with silicone grease to allow easy

removal of the samples after curing. The cure of the samples were as follows: initial gelation for 4 hours at 55°C (131°F) followed by 2 hours at 120°C (248°F) and then 2 hours at 177°C (350°F). After cure, the samples were removed from the aluminum foil cups and wiped with acetone to remove any residual lubricant; any surface irregularities were removed with a scalpel. The samples were weighed and then esposed to 150°C and 1 x 10^{-6} mm Hg for 210 hours. Weight losses were determined at 24-hour intervals as described above. No mass spectroscopy data were obtained on these samples. The data are shown in Table VII.

Effect of Postcuring Conditions on the Thermal Vacuum Properties of Epon 422J

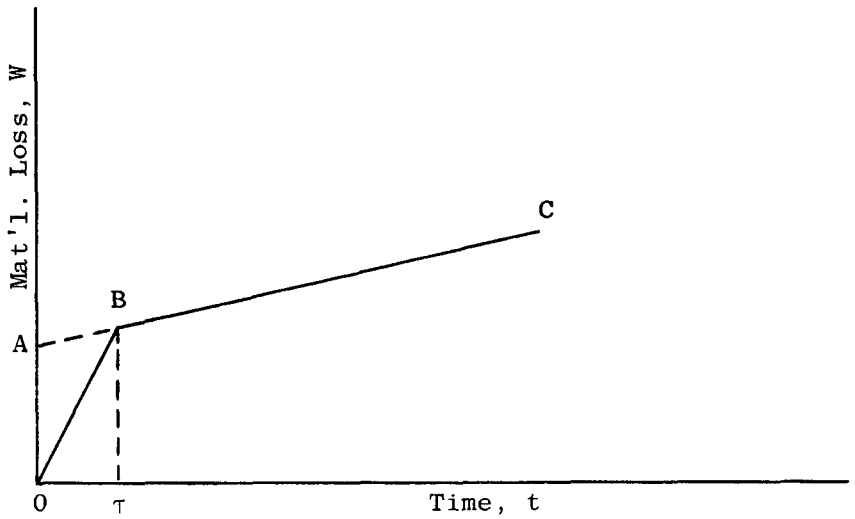
Test specimens of Epon 422J were prepared and cured as described above, then postcured under several selected conditions: (1) at 350°C for 6-48 hours in air; (2) at 350°C for 6-48 hours under nitrogen. During the postcure cycle, the sample under nitrogen lost 0.00631 g or 0.19% of its original weight, while that in air lost only 0.088% of its original weight. However, the latter samples underwent a marked darkening in color. Samples were vacuum tested at 200°C as described above.

RESULTS

The Shell Epon adhesives examined in this study are tabulated in Table I along with a brief description of their composition and the approximate size and weight of the sample degraded. In general, the weight loss of heterogeneous materials under vacuum is dependent on temperature, the amount and type of volatile material present in the sample, and the geometry of the sample. At pressures below about 10^{-2} mm Hg, weight loss is not usually considered sensitive to pressure. In this report, weight losses are reported both as percent loss on the basis of original sample weight, and as over-all loss per unit surface area (g cm^{-2}) of sample. The significance of reporting both parameters will become evident later in the test. Some other terms used in

reporting outgassing data are defined below.

A plot of material loss versus time is generally of the form:



Steady State (SS) is represented by the linear portion (BC) of the curve.

Initial Weight Loss is the zero-time intercept of the linear portion of the weight loss curve (A).

Time Until Steady State is the time before the weight loss becomes linear (τ).

Steady State Loss Rate is given by the slope of the linear portion of the weight loss curve ($\frac{\Delta W}{\Delta T}$).

All these parameters are estimated graphically.

Sample weights are determined with an uncertainty of ± 5 in the fifth decimal place (about ± .005% in most cases). However, as weight losses are generally of the order of 1-5% of the total sample weight, the actual error in weight loss measurements is at least 0.5%; a conservative range of error may be set at 0.5 - 1.0%.

The parameters estimated graphically are rather less accurate; initial weight losses are accurate to about 5%. Weight loss rates are approximately two orders of magnitude smaller than the actual weight losses and are accordingly less precise. The times to steady state are approximations, because a sharp transition to the steady state is rarely observed.

The weight loss data for all the epoxies tested are summarized in Tables II - V and plotted in Figs. 4-7. Tables II and IV summarize the weight loss data at 150° and 200°C respectively, and Tables III and V summarize the information obtained on the outgassed material at 150° and 200° respectively. Figure 4 gives percent weight loss as a function of time at 150°C. Figure 5 illustrates the same data calculated as weight loss per unit surface area. Figures 6 and 7 show the corresponding data obtained at 200°C.

Effect of thickness on weight loss properties: The effect of thickness of Epon 914 samples on its weight loss characteristics at 150°C is shown in Figs. 8-12. The data are summarized in Table VI.

Effect of material purity on weight loss characteristics: The weight loss curves for the synthetic epoxide adhesives (analogs of the Epons), prepared to determine the relationships between catalyst purity and base polymer purity, are shown in Fig. 13 and the data tabulated in Table VII.

Effect of postcuring on the outgassing properties of Epon 422J: The following figures summarize the effects of various postcuring procedures on the outgassing characteristics of Epon 422J at 200°C and 10^{-6} mm Hg. Figure 14 compares the weight loss curve of Epon 422J which was not postcured with weight loss curves for the same material postcured at 177°C (350°F) for 6, 12, and 48 hours in air and for 48 hours in nitrogen. Figure 15 shows the percent weight loss as a function of the postcure time for the same samples which had been exposed to 200°C and 10^{-6} mm Hg for 48 hours. Because the samples employed were of nearly the same thickness and surface area, plots for the same information in terms of weight lost per cm^2 are not included.

Table II

OUTGASSING CHARACTERISTICS OF THE SHELL EPON ADHESIVES

WEIGHT LOSS DATA AT 150° C

Adhesive No.	Sample Thickness g/unit area	Initial Weight percent	Loss $g\ cm^{-2} \times 10^{4}$	Steady State Loss Rate $g\ cm^{-2}\ hr^{-1} \times 10^{6}$
934	1.47	1.18	7.7	1.2
914	2.16	0.49	4.6	0
931	1.88	0.61	4.4	0
901-B3	--	--	--	--
903	0.477	0.78	1.6	0.21
917	0.816	1.35	4.6	0.94
941	0.872	1.10	3.5	0.6
422J	0.990	3.97	17.1	1.28
924	0.443	3.18	5.4	1.2

Table III

SUMMARY OF MASS SPECTROSCOPY DATA OF VOLATILE SPECIES (Mole Percent)
(150°C and 10^{-6}mm Hg)

Epon Adhesive	CO_2	H_2O	O_2	Acetone	Toluene	Methanol	N_2	Benzene	Aldehydes	$MeCl_2$	C_5 Hydrocarbon	NH_3
934	73.0	7.6	2.6	2.0	2.3	---	12.5	---	---	---	---	---
914	95.4	2.6	0.4	---	---	---	1.6	---	---	---	---	---
931	---	91.3	1.1	1.5	---	0.7	5.4	---	---	---	---	---
901-B3	---	---	---	---	---	---	---	---	---	---	---	---
917	93.2	4.3	0.4	0.2	---	---	1.6	0.2	---	0.1	---	---
941	94.8	3.0	---	---	---	---	---	0.04	---	---	2.2	---
422J	92.1	5.0	0.4	0.7	---	---	1.6	0.1	---	0.1	---	---
924	93.3	3.6	---	3.1	2.3	---	---	1.3	---	3.8	---	---
903	93.5	3.9	0.3	0.3	---	---	1.5	0.4	---	0.1	---	---

Table IV

OUTGASSING CHARACTERISTICS OF THE SHELL EPON ADHESIVES

WEIGHT LOSS DATA AT 200° C

Adhesive No.	Sample Thickness g/unit area	Time to Steady State hours	Initial Weight Loss		Steady State Loss Rate g cm^{-2} hr^{-1} 10^6
			percent	g cm^{-2} x 10^4	
934	1.48	80	2.22	16.3	8.6
914	2.04	100	1.84	13.7	9.6
931	1.89	120	2.23	15.2	6.3
901-B3*	1.03	15	0.51	2.7	2.5
903	0.396	70	1.77	2.8	1.2
917	1.09	30	2.70	11.8	0.8
941	1.13	100	2.29	10.5	3.9
422J	0.964	20	4.40	17.9	0.8
924	0.277	20	5.51	5.5	4.8

*Pretreated with 10^{-6} vacuum for 55 hrs at ambient temp.

Table V

SUMMARY OF MASS SPECTROSCOPY DATA OF VOLATILE SPECIES (Mole Percent)
(200°C and 10^{-6}mm Hg)

Epon Adhesive	CO_2	H_2O	O_2	Acetone	Tuolene	Methanol	N_2	Benzene	Aldehydes	$MeCl_2$	C_5 Hydrocarbon	NH_3
934	89.1	9.1	---	---	1.1	---	---	0.1	---	---	---	---
914	96.5	2.5	---	0.3	0.7	---	---	0.02	---	---	---	---
931	0.4	92.3	---	1.2	0.4	1.6	---	---	4.1	---	---	---
901-B3	92.7	3.7	0.4	0.8	---	---	2.2	0.02	---	0.1	---	---
917	61.2	27.4	---	2.8	---	---	---	---	8.6	---	---	---
941	76.4	19.6	0.4	2.1	---	---	1.5	0.02	---	---	---	---
422J	----	66.3	0.3	---	---	---	1.7	0.1	---	---	---	12.8
924	64.0	28.1	0.3	3.1	---	---	---	0.02	---	---	---	---
903	0.7	99.2	---	---	---	---	---	---	---	---	---	---

Table VI

OUTGASSING CHARACTERISTICS OF EPON 914
FOR TEST SPECIMENS OF VARIOUS THICKNESSES

Sample Thickness mils	Initial Weight Loss		Steady State Loss Rate $g\ cm^{-2}\ hr^{-1} \times 10^{6}$
	percent	$g\ cm^{-2} \times 10^{4}$	
3.83	0.95	2.28	0.04
2.75	1.07	1.82	0.03
1.33	1.26	1.02	0.04
0.34	2.24	0.48	0.04

Table VII

EFFECT OF COMPONENT PURITY ON THE OUTGASSING CHARACTERISTICS OF SYNTHETIC EPOXIDE ADHESIVE ANALOGS

Resin System		Initial Weight Loss (%)	Weight Loss Rate g cm^{-2} hr^{-1} x 10^6	Weight Loss at 100 Hrs.
Epoxide	Amine			
Impure	Impure	0.5	20.9	2.0%
Pure	Impure	0.3	14.4	1.8
Impure	Pure	0.6	4.0	1.0
Pure	Pure	0.33	3.4	0.66

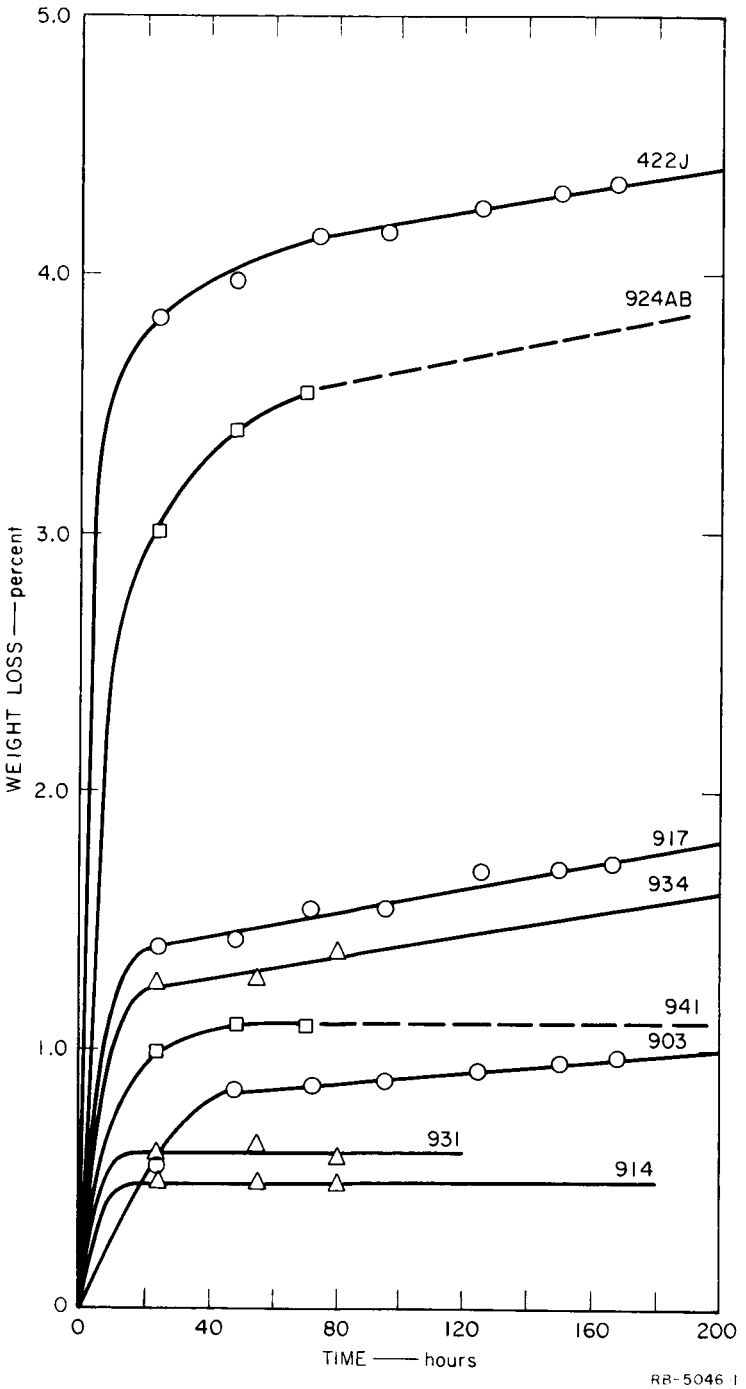


FIG. 4 PERCENT WEIGHT LOSS OF EPON ADHESIVES AT 150°C AND 10^{-6} mm Hg

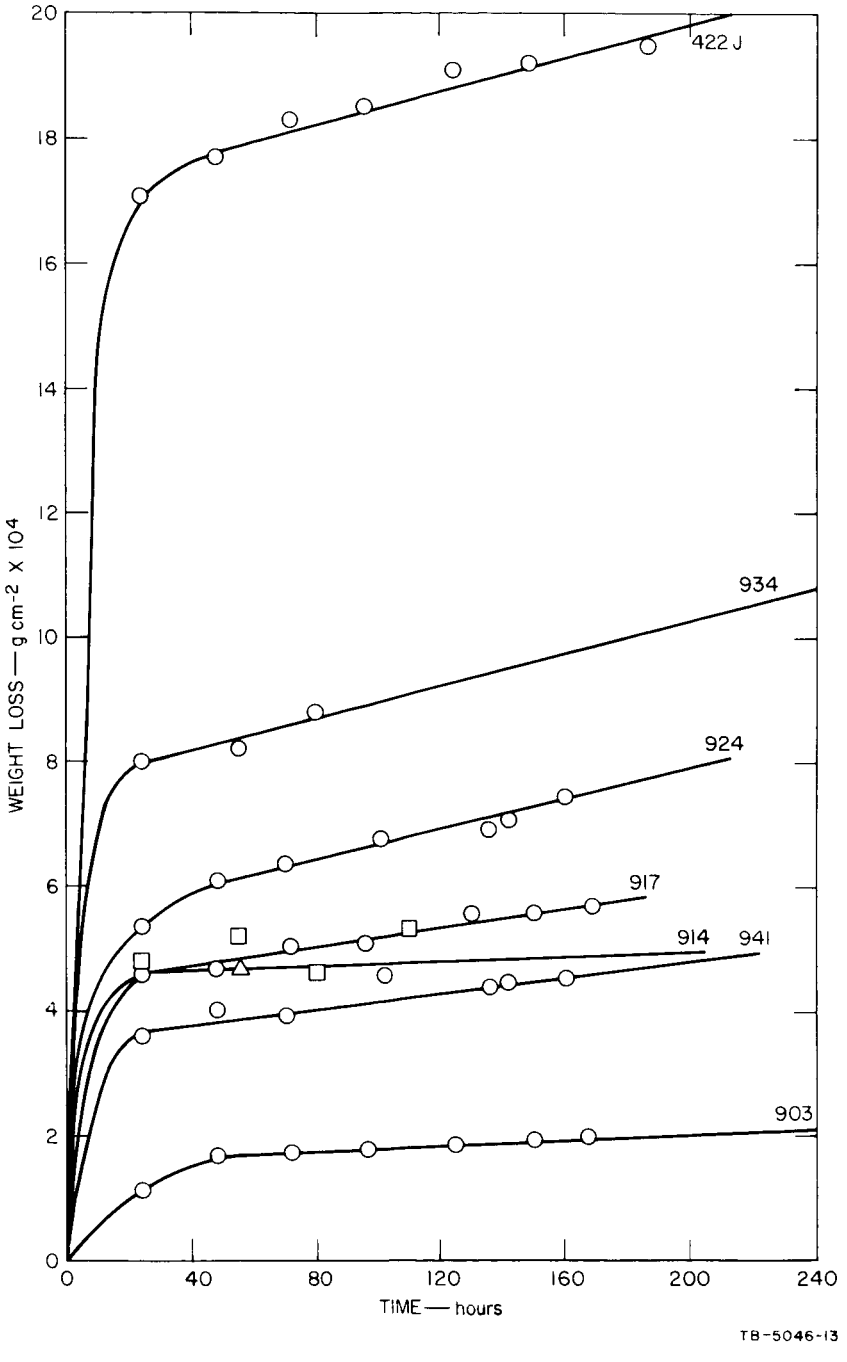


FIG. 5 WEIGHT LOSS OF EPON ADHESIVES IN g cm^{-2} AT 150°C AND 10^{-6} mm Hg

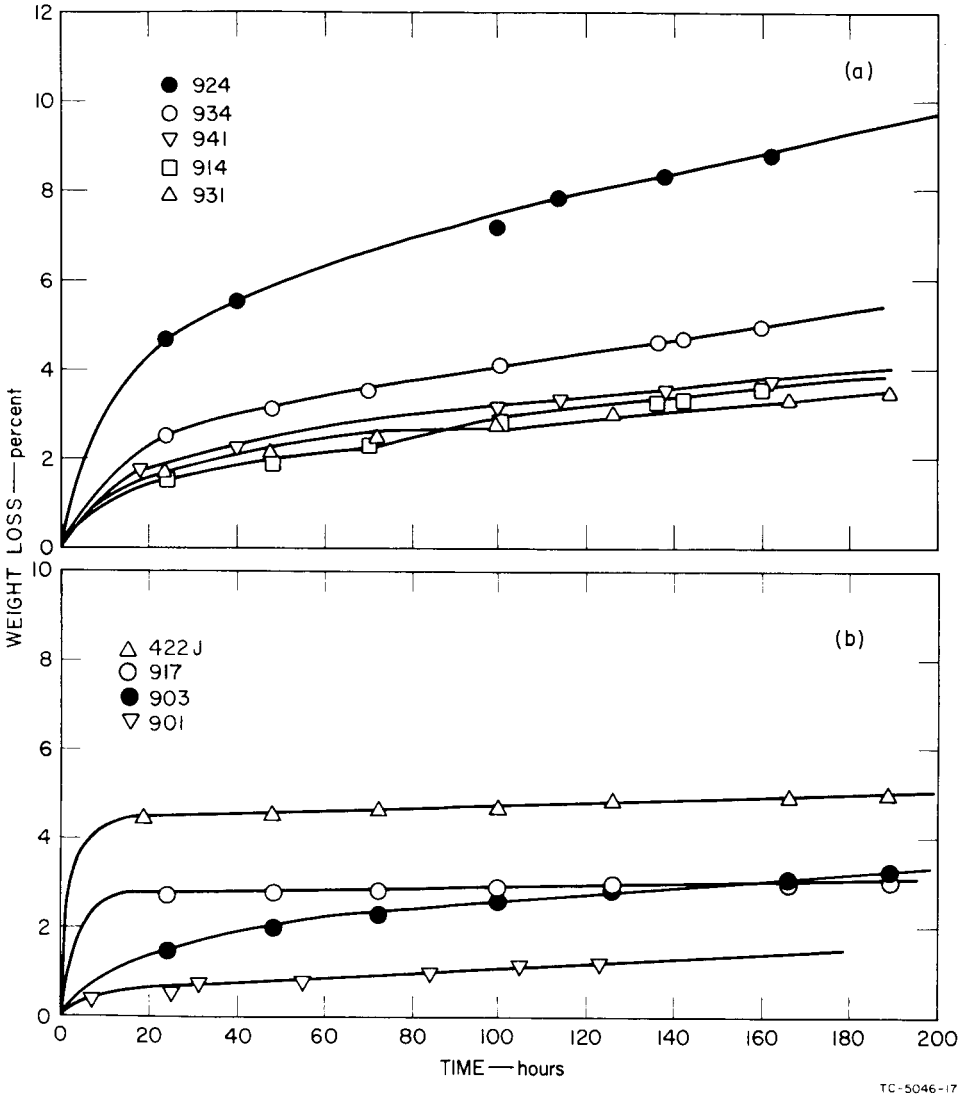


FIG. 6 PERCENT WEIGHT LOSS OF EPON ADHESIVES AT 200°C AND 10^{-6} mm Hg

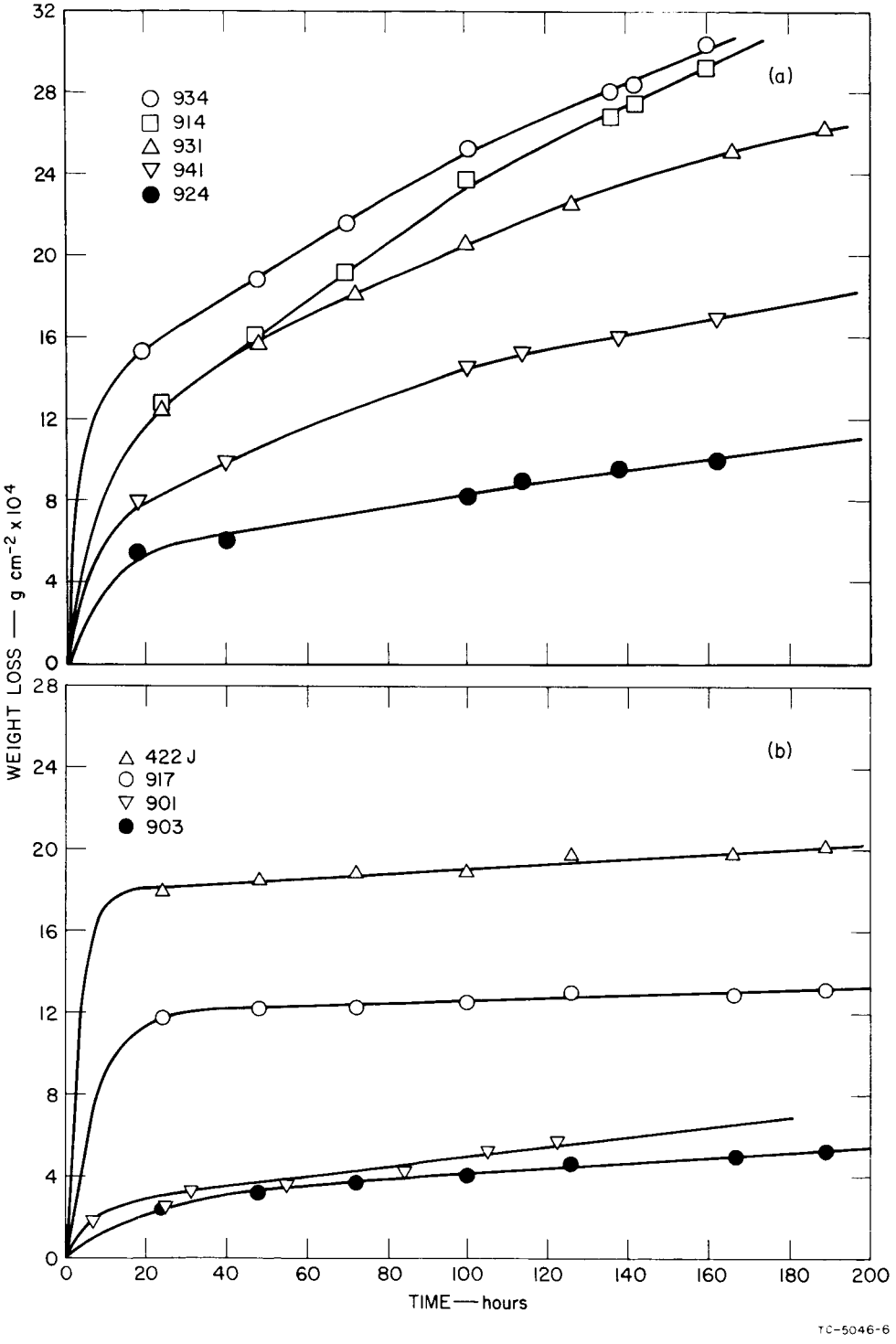


FIG. 7 WEIGHT LOSS OF EPON ADHESIVES IN g cm^{-2} AT 200°C AND 10^{-6} mm Hg

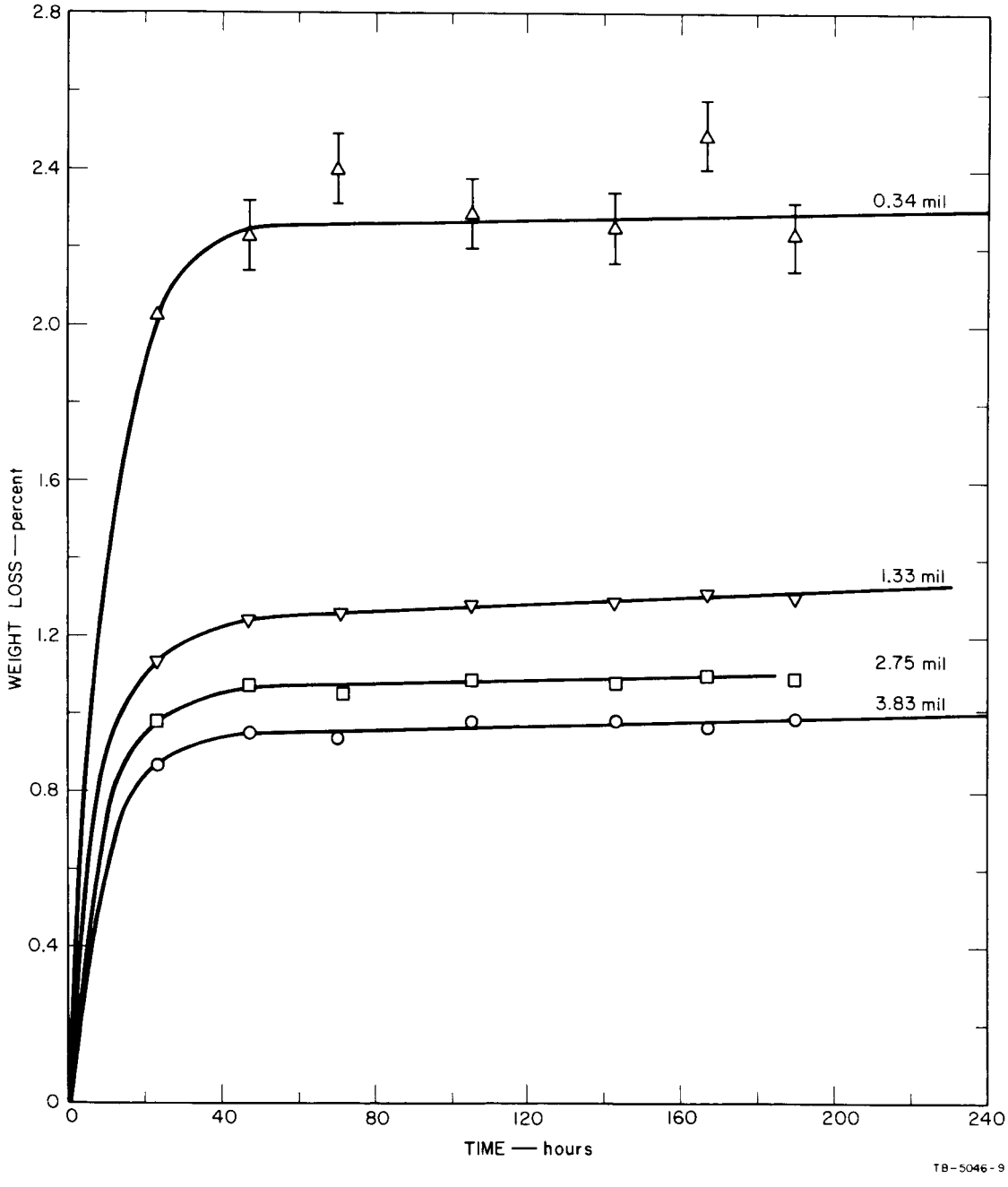


FIG. 8 PERCENT WEIGHT LOSS FOR TEST SPECIMENS OF DIFFERENT THICKNESSES AT 150°C AND 10^{-6} mm Hg

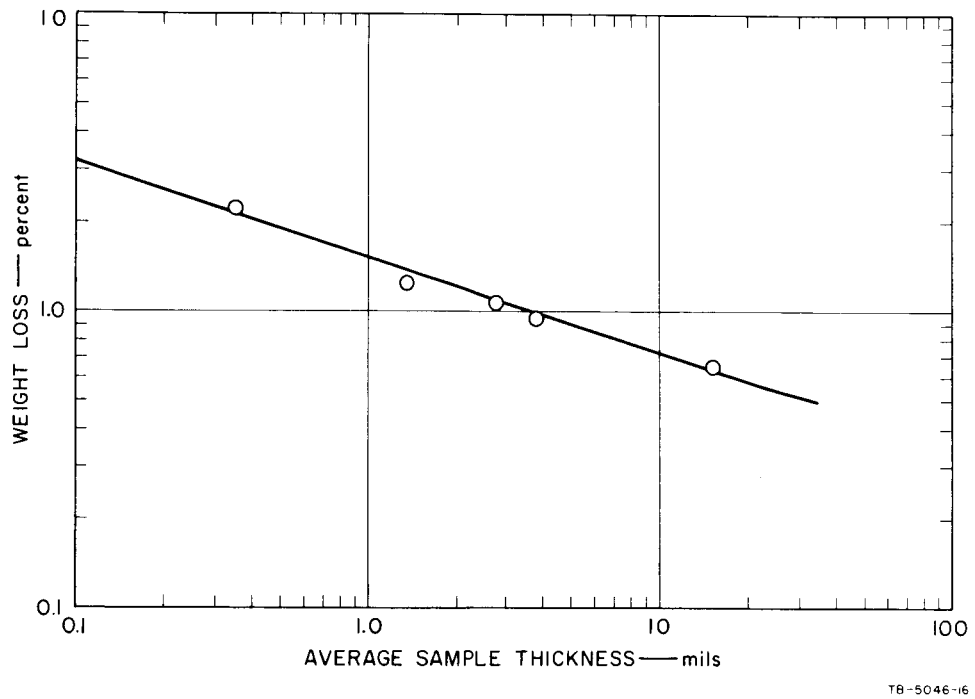


FIG. 9 EFFECT OF SPECIMEN THICKNESS ON CUMULATIVE PERCENT WEIGHT LOSS AFTER 48 HOURS AT 150°C AND 10^{-6} mm Hg

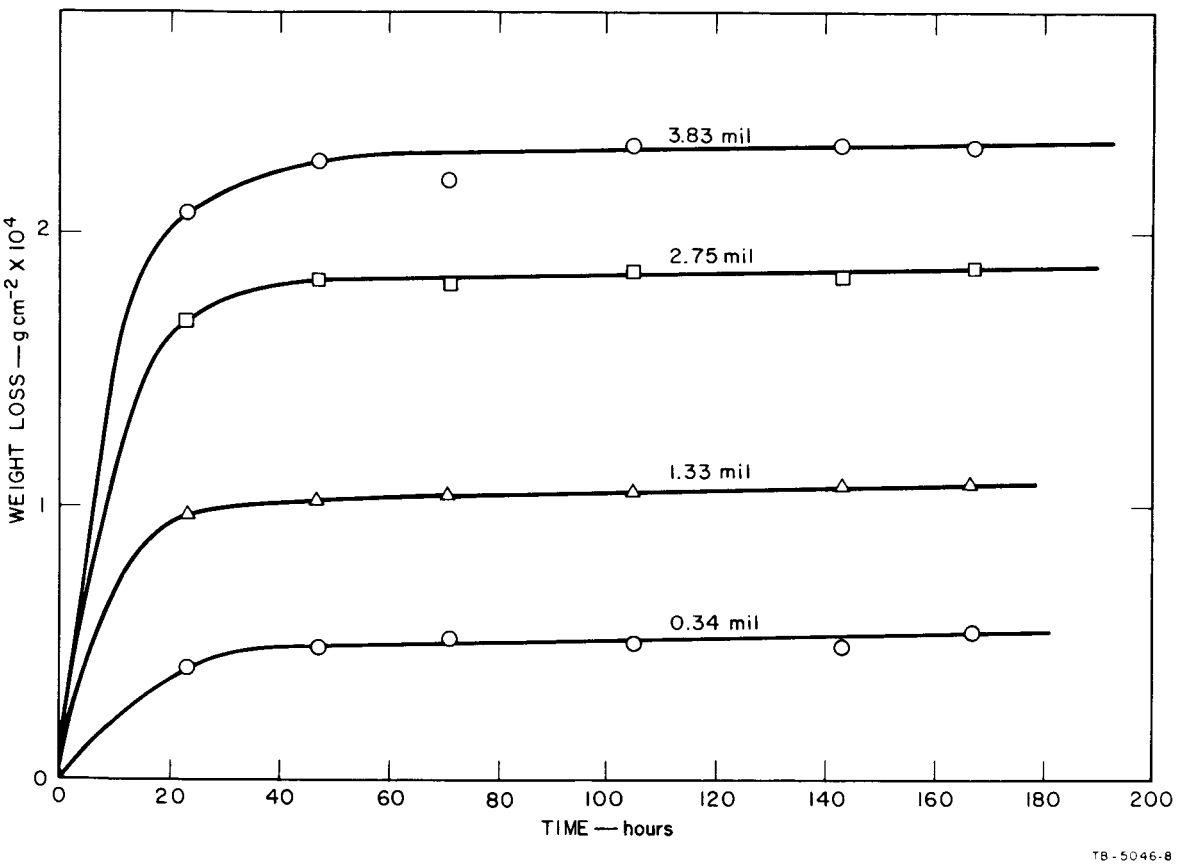


FIG. 10 WEIGHT LOSSES IN g cm^{-2} FOR TEST SPECIMENS AT DIFFERENT THICKNESSES

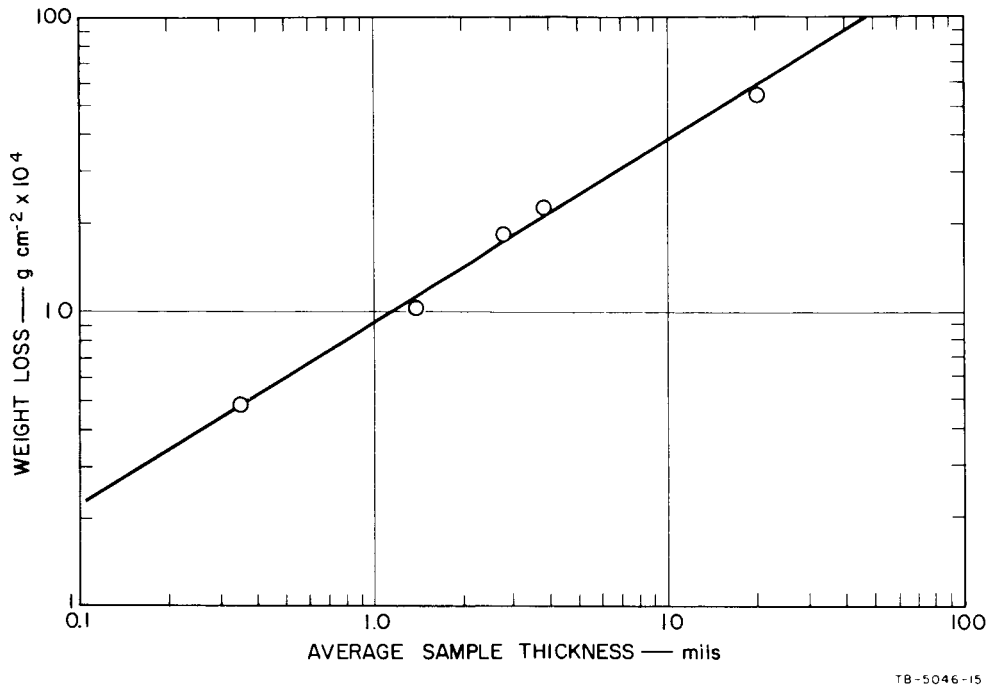


FIG. 11 EFFECT OF SPECIMEN THICKNESS ON CUMULATIVE WEIGHT LOSS (g cm^{-2}) AFTER 48 HOURS AT 150°C AND 10^{-6} mm Hg

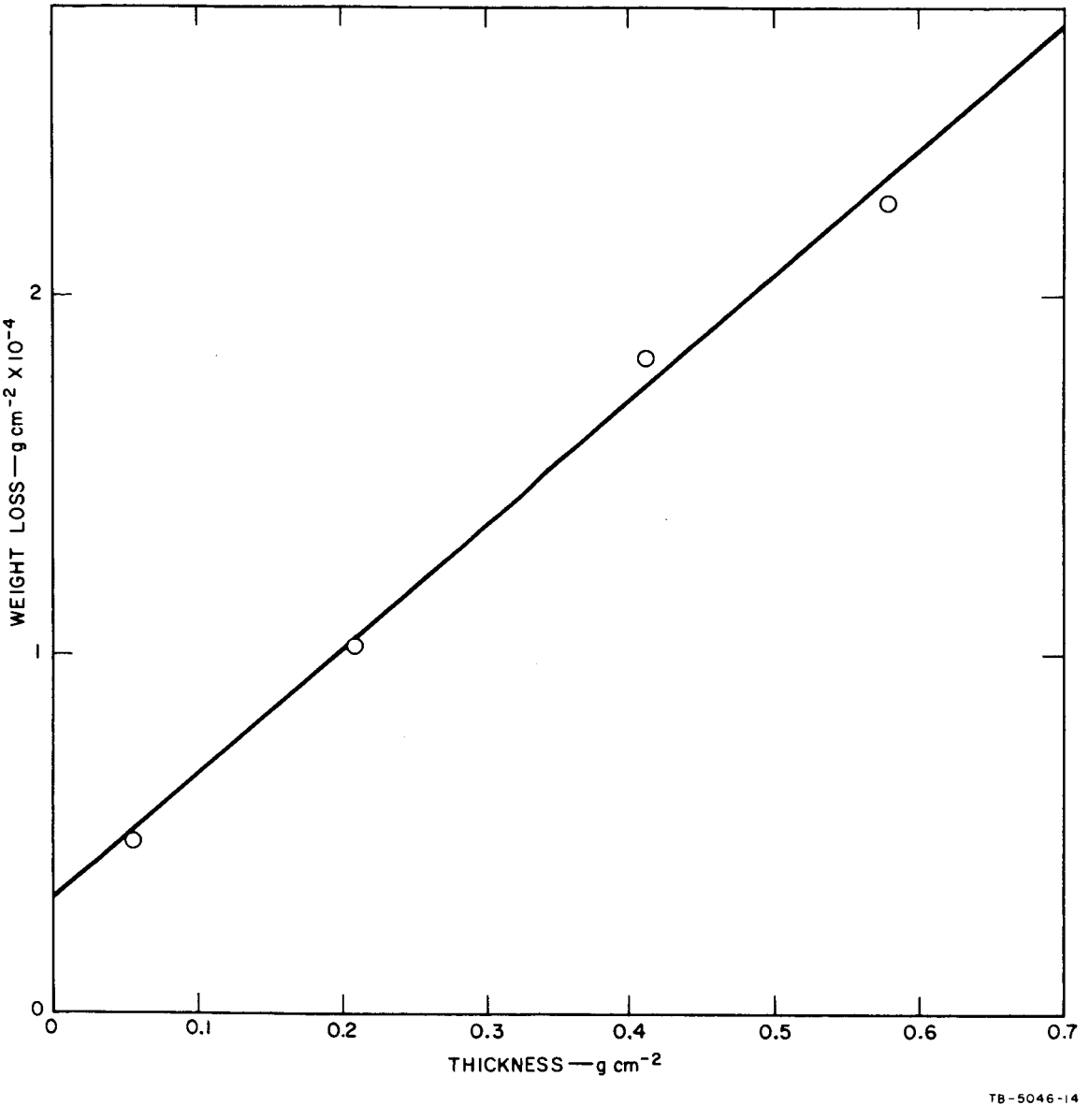


FIG. 12 EFFECT OF SPECIMEN THICKNESS (0.3-4.0 mils) ON CUMULATIVE WEIGHT LOSS — LEAST SQUARES APPROXIMATION

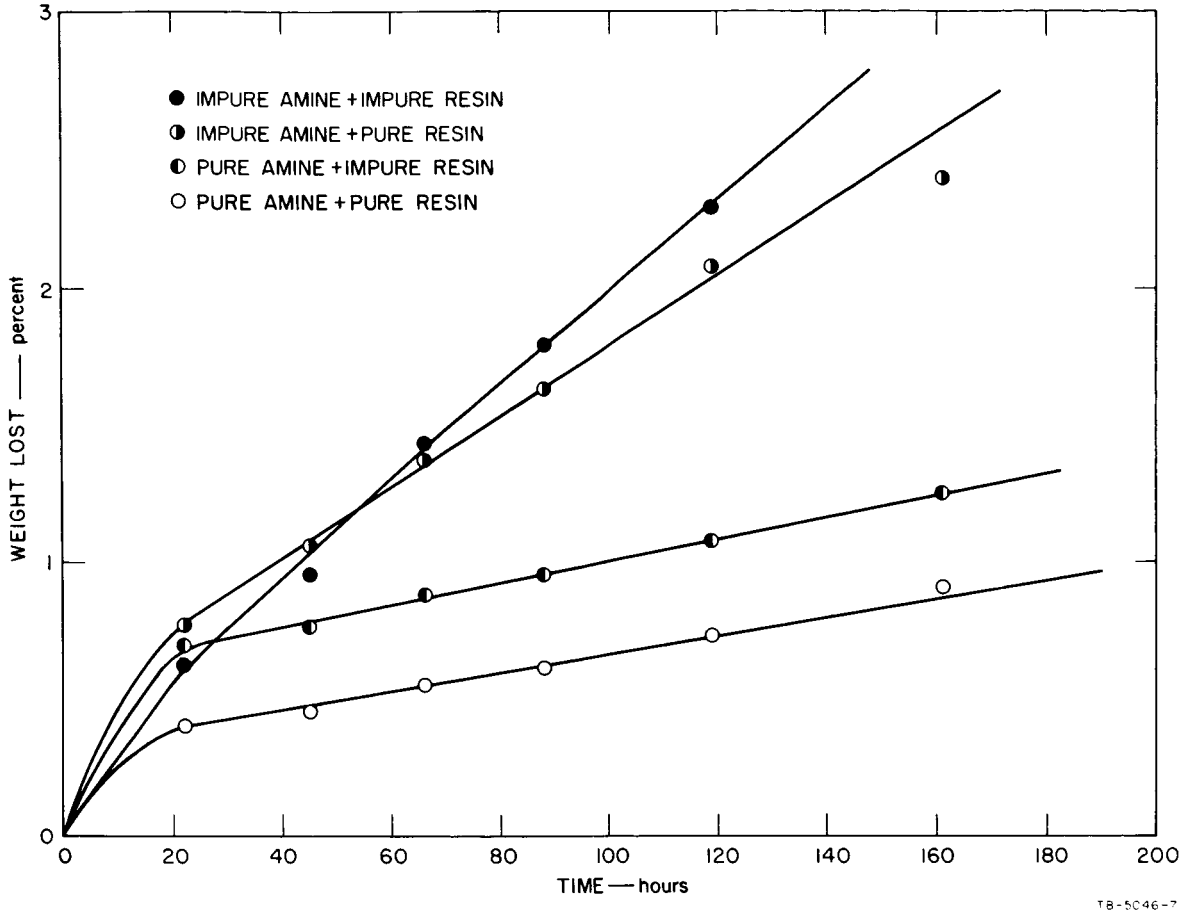


FIG. 13 PERCENT WEIGHT LOSS OF ANALOG RESIN SYSTEMS OF DIFFERENT DEGREES OF PURITY AT 200°C AND 10^{-6} mm Hg

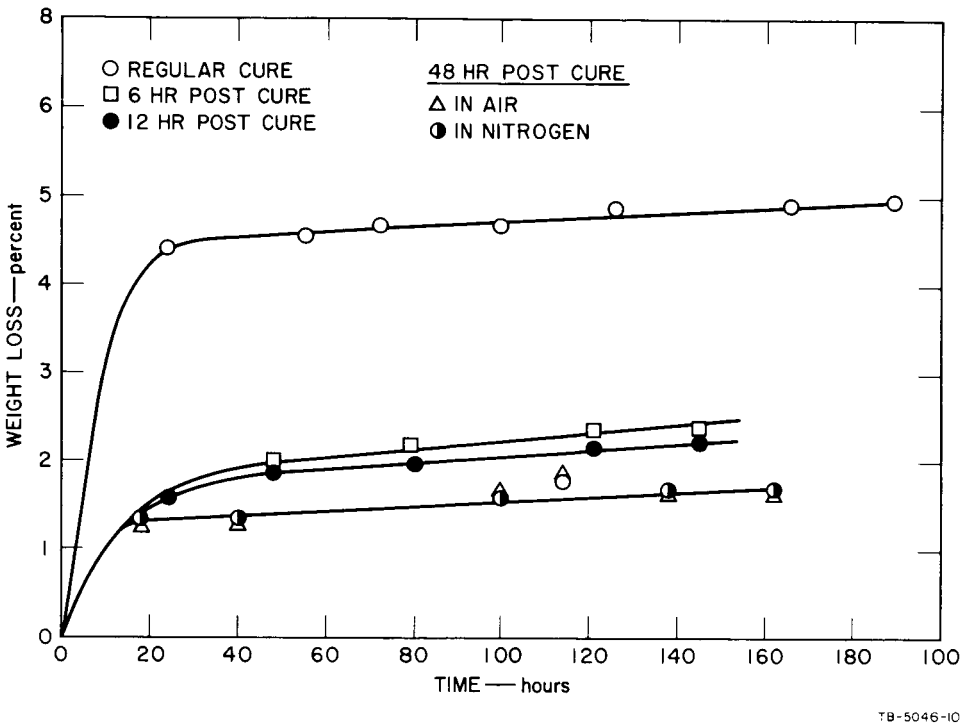


FIG. 14 PERCENT WEIGHT LOSS OF EPON 422J AFTER VARIOUS POSTCURING CONDITIONS

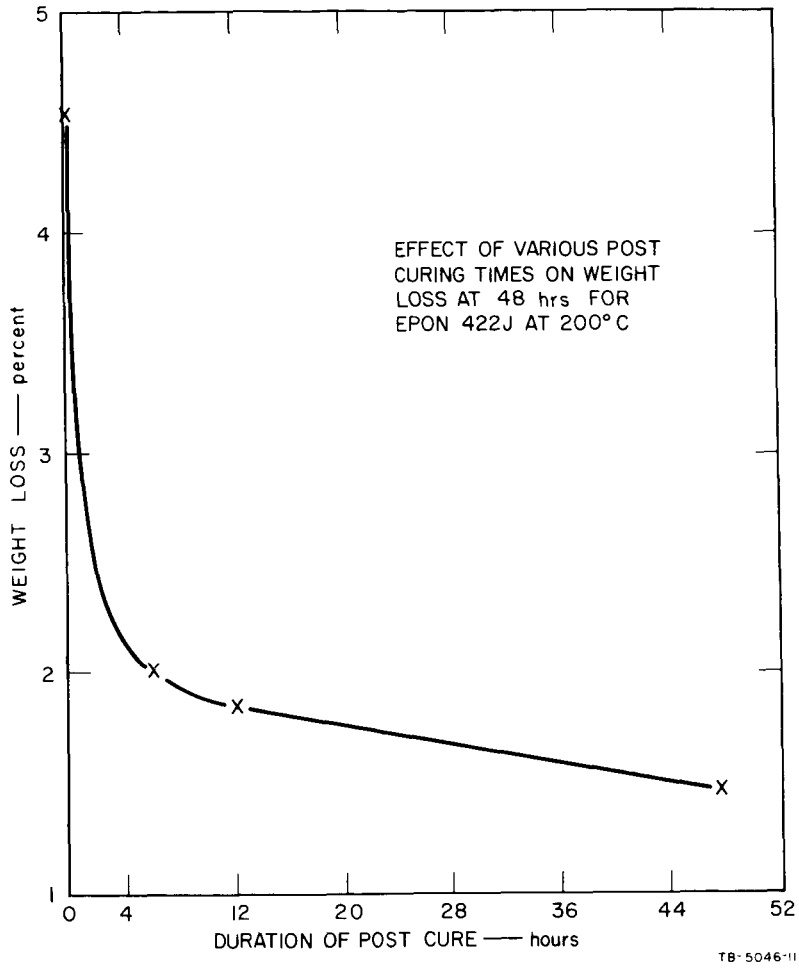


FIG. 15 EFFECT OF DURATION OF POSTCURE ON THE CUMULATIVE PERCENT WEIGHT LOSS AFTER 48 HOURS AT 200°C AND 10^{-6} mm Hg

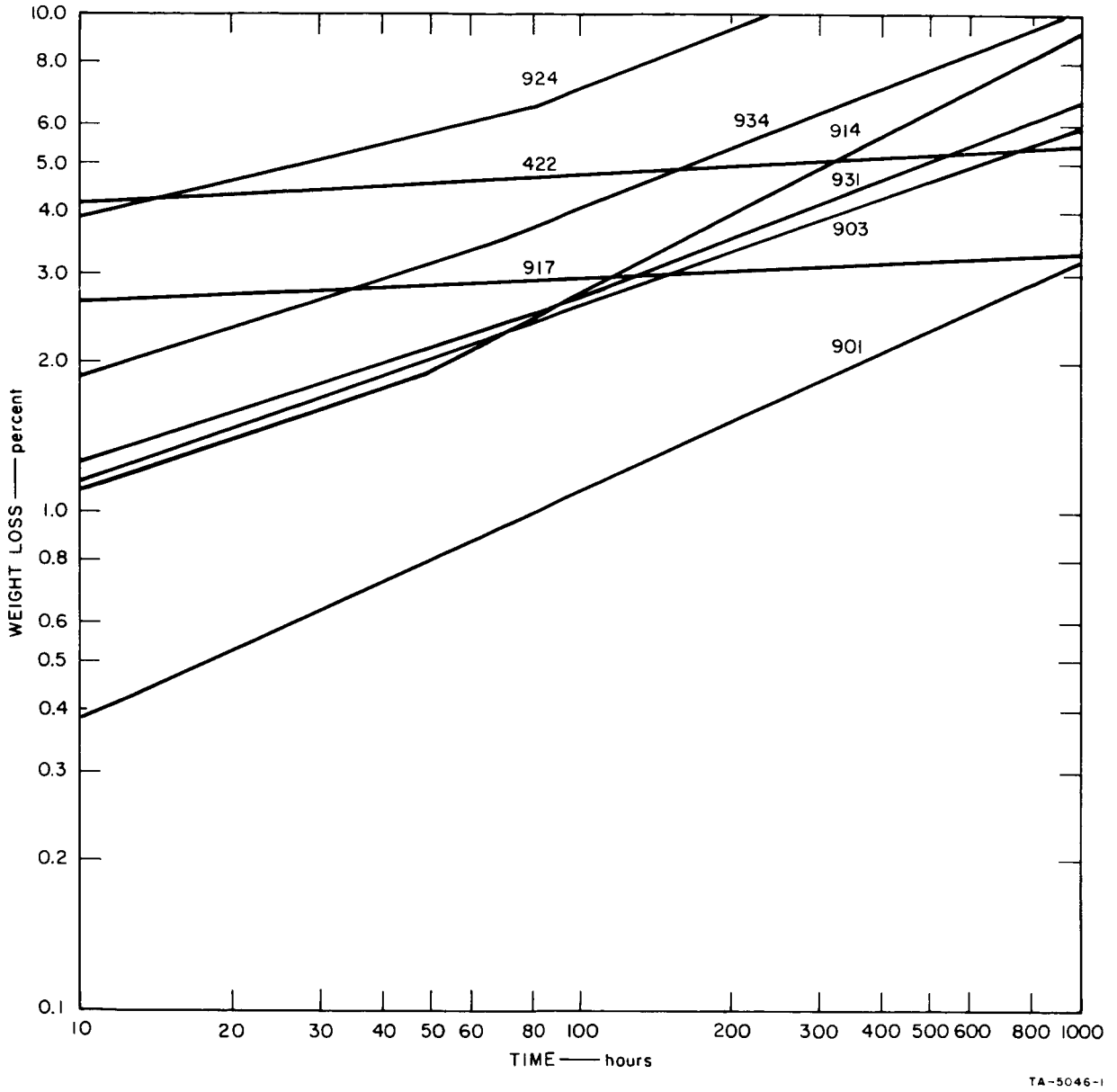


FIG. 16 LOGARITHMIC RELATIONSHIP OF WEIGHT LOSS DATA FOR EPON ADHESIVES AT 200°C AND 10^{-6} mm Hg

DISCUSSION

Epoxy adhesives have been.widely used for both structural and non-structural applications in spacecraft. A brief description of the general chemistry of these materials is given in the Appendix. Of particular importance to the JPL materials specification program have been the structural adhesives as represented by the Shell "Epon" adhesives. In the first phase of this program the general thermal-vacuum stability and the outgassing characteristics of these materials were determined.

Of the eleven Shell "Epon" adhesives initially selected by JPL cognizant engineers, three were eliminated after joint discussions with the JPL cognizant engineer Hugh Maxwell and Mr. Evan Blake of the Shell Chemical Co. These were Epon 911, which contains a polysulfide in its formulation; and Epons 941 and 929, which have less quality control and are, therefore, cheaper products (these two are similar to Epon adhesive 934 which is a high-grade material). It was of interest to note, however, that in preliminary screening the sample of Epon 941 received performed quite favorably compared to the other materials. The remaining eight samples (Epon 901-B3, 903, 914, 917, 924, 931, 934, and 422J) were then prepared and cured and exposed to a thermal-vacuum environment to determine the amount of outgassing. In addition, the outgassed material was analyzed to determine its source, i.e., polymer chain degradation, additives, etc.

The shape of the curves obtained from weight loss data indicate that a large amount of weight is lost initially, often within the first 24 hours, and then the loss of weight levels off, and varies linearly with time. This behavior is generally interpreted as the rapid removal of material adsorbed on the surface of the sample (such as air and H_2O), followed by the much slower diffusion of low molecular weight material such as residual solvent and unreacted fragments from the interior polymer network. It is realized, of course, that this treatment is an oversimplification. In fact, no real separation of "surface" and

"diffusion" processes can be made, and the so-called "initial weight loss" must necessarily include loss due to diffusion of materials having low bonding energies (e.g., gases) and volatile liquids (e.g., solvents). In practice, however, two parameters, the initial weight loss and the weight loss rate, are sufficient to describe the thermal-vacuum behavior of the samples, especially if information on the initial behavior of the material is of no particular interest.

At 150°C all the epoxies tested reached steady state within 48 hours. The weight loss curves of the Epon adhesives at this temperature are shown in Figs. 4 and 5, and the data are tabulated in Table II. None of the Epon adhesives exhibited any sign of degradation at this temperature with the possible exception of Epon 934 which darkened in color slightly. Outgassing products, as determined by mass spectroscopy, were primarily CO_2 (90-95 mole %) and water (2-10 mole %), with trace amounts of solvents such as acetone, toluene, and benzene.

During the initial exposure (24 hours) to the 200°C environment the behavior of the Epon samples was similar to their behavior at 150°C. Although there was an increase in the total amount of material lost, the relationship among the Epons remained the same:

% range	150°C	% range	200°C
0-1.0	914	0-1.75	901
	903		903
	931		914
			941
1.0-1.5	941	1.75-2.75	941
	934		934
	917		917
3.0-4.0	924	4.0-5.0	422J
	422J		924

After this initial 24-hour period, large differences in behavior occurred. The times to achieve steady state increased greatly and some materials appeared to equilibrate only after 80 hours or more. Marked increases in the rates of weight loss were also observed. Data are tabulated in

Table IV and illustrated in Figs. 6 and 7. Epon 934 provides an excellent example of this trend. At 150°C, this adhesive achieved steady state in less than 24 hours and had a loss rate of 1.2×10^{-6} g cm^{-2} hr^{-1}. At 200°C, it required over 80 hours to reach a steady state and the rate had risen to 8.2×10^{-6} g cm^{-2} hr^{-1}. Also at this temperature a considerable quantity of a viscous brown oil was observed to condense in the head of the resin kettle, indicating degradation of this resin. Epons 914 and 931, which also appeared to undergo degradation, behaved in a similar manner. Epon 924 and 941 may also degrade slightly at 200°C and their rates are also considerably larger than those observed at 150°C. Time to steady state is variable at 200°C, ranging from 20 hours for Epon 924 to as high as 120 hours for Epon 931.

The behavior of Epon 903 is somewhat ambiguous: Although it shows a very low initial weight loss, it achieves steady state only after about 60 hours. Its steady state weight loss rate is low, 1.2 g cm^{-2} hr^{-1}. There was no evidence of oil evolution and little color change in the test specimen.

The remaining two adhesives, Epons 917 and 422J, achieve steady state fairly rapidly, and exhibit low steady state loss rates. They show no signs of degradation. In fact, the value of 0.8×10^{-6} g cm^{-2} hr^{-1} observed for both materials is actually lower than their respective values of 0.94 and 1.28×10^{-6} at 150°C. It has been found that the large initial weight loss of the Epon 422J may be greatly reduced by postcuring the resin.

In general, the weight losses of the Epon adhesives at 150°C follow very closely a desorption type of curve, i.e., a good straight-line relationship is obtained within a short time, generally within 24 hours of treatment. This is not the case at 200°C. In several of the adhesives, material degradation takes place within the polymer network, and the diffusion of these degradation products plays an important role in the total outgassing process. When weight loss curves of these materials were plotted on a linear scale, it was difficult to ascertain just when a steady state was reached, and in several cases whether it

was achieved at all. An alternative method of plotting the data is to use the logarithmic form

$$\text{Weight Loss, } W = at^b$$

where a and b are constants. The constants a and b for the epoxy adhesives at 200°C and 10^{-6} mm are tabulated below, as well as the constant b' (i.e., the constant for the second slope) for those adhesives that exhibit a change in slope.

Epon Adhesive	a	b	b'
924	2.32%	0.237	0.561
4225	3.56%	0.065	---
917	2.30%	0.053	---
934	0.96	0.307	0.403
941	0.82	0.265	0.393
903	0.46	0.385	---
914	0.51	0.344	0.515
931	0.58	0.337	0.384
901-B3	0.13	0.463	---

This form has the mathematical advantage in that W = 0 at t = 0, thus giving a more realistic description of the total outgassing process.

When the 200°C data were plotted on a full logarithmic scale, good straight lines were obtained (Fig. 16). In the case of several of the adhesives that had large weight losses, abrupt increases in the slopes were noted. This effect is most clearly illustrated by Epon 924 where there is a distinct change in slope at approximately 80 hours. The exponential rate of loss rises to $t^{0.6}$ from $t^{0.24}$. Rivera, et al.,[2] have observed a similar effect for Epon 820 CL at 10^{-9} mm Hg and 25°C. They attribute this to a change in loss mode or species. In the case of the adhesives tested here, however, the situation seems clear. Because none of these transitions in slope is observed at 150°C, it is reasonable to assume that those observed at 200°C are due to diffusion products or degradation or to chain scission of the polymer. Although these fragments may be produced early in the thermal vacuum treatment, they will consist,

[2]M. Rivera, W. M. Fassell, Jr., and J. Jensen, Trans. Natl. Vac. Symp. 9, 342 (1962).

at least in part, of moderately long chains, and the time required for diffusion of these chains will be large.

This interpretation is consistent with the fact that all the materials exhibiting this transition also gave visual evidence of material degradation such as oil evolution and sample darkening.

In most cases, the amount of degradation material was too small to isolate, and was observed only as a dark oily film formed around the top of the resin pot. In the case of the Epon 934 and 931 adhesives, sufficient amounts of degradation product were available for infrared spectra. Both give very similar spectra. They may be identified tentatively as aromatic esters on the basis of absorptions at 5.80, 7.95, and 9.30μ. The product of the 931, however, exhibits an additional sharp band at 6.65μ and a broadening in the 9-10μ region. The base epoxy materials of the Epon 934 and 931 are identical, with a polyamide as curing agent for the former and an aromatic amine for the latter. The materials obtained in thermal-vacuum treatment do not correspond to unreacted starting material, but are evidently products of epoxy degradation.

Mass spectroscopy data were somewhat disappointing. In the case of Epon 934, where breakdown of the adhesive seemed obvious, no outgassing products were found except CO_2, water, and solvent. The same was the case for 914. In the case of Epon 931, acetaldehyde and propylaldehyde were reported, but only in very small amounts. Trace amounts of aldehydes were also reported in samples of Epon 917, but there were no other indications of degradation with this material.

Effect of Postcuring on the Thermal Vacuum Behavior of Epon 422J

In the thermal vacuum treatment of Epon 422J it was found that this adhesive exhibited not only a larger initial loss of weight than the other adhesives tested at 150°C but a larger rate of loss after induction. At 200°C, however, this adhesive behaved differently from the other adhesives, i.e., although the initial weight loss was similar to that at 150°C (4.43% in the first 24 hours), the loss in weight levelled off,

so the final weight loss was only 4.97% after 189 hours, and increase of only 0.54% in 145 hours. Also, at 200°, Epon 422J showed no evolution of oily material into the head of the resin pot. The only product indicative of possible degradation was ammonia (12.8 mole percent from mass spectroscopy data).

Since Epon 422J is a fiberglass-based tape type adhesive especially developed for high temperature use, JPL expressed interest in rendering this material more suitable for use in the space environment. It was felt that despite its large initial weight losses at 150° and 200°, this adhesive was not actually undergoing degradation or chain scission. It is noted in the Epon Adhesives Manual distributed by Shell Chemical Division that Epon 422J "cures with the evolution of volatiles and thus forms a porous bond..." Therefore incomplete curing coupled with the high porosity of the material provides a ready explanation of the anomalously large amount of volatiles observed. It was concluded from this, as well as our own experiments, that the properties of this resin could be greatly improved by postcuring the samples at temperatures greater than 150°C.

Test samples were postcured in air and under a nitrogen atmosphere (48 hours at 177°C) to see if any oxidative effects would be observed. On testing these samples, it was found that they behaved identically under thermal-vacuum exposure, yielding weight loss curves that were indistinguishable within experimental error (Fig. 14). Both showed a marked reduction in weight loss over the untreated sample; for example, after 160 hours the postcured samples had lost only 1.7% of their original weight, compared with 5.0% for the untreated sample. It is interesting to note that mass spectroscopic analysis of the outgassing products consisted of only 3.4 mole percent NH_3 from the nitrogen-postcured sample and none from the air-postcured sample.

Since these experiments indicated that postcuring definitely improved the thermal-vacuum characteristics of the Epon 422J material it was of interest to determine the minimum time necessary for obtaining a satisfactory material. The data are plotted in Fig. 15. Although

a 48-hour postcure does give the best results, postcuring periods as short as 6 hours at 177°C are sufficient to improve the vacuum outgassing characteristics of this resin, making it superior in performance at 200°C to the other adhesives. In addition, postcuring in air appears to be as satisfactory as postcuring in an inert atmosphere, and perhaps even preferable in view of the elimination of NH_3 from the outgassing products. Although no testing of the postcured samples were made at 150°C, it is reasonable to assume that the effects would be similar and might reduce the rather large steady state loss rate observed at this temperature. This steady state loss rate appears to be temperature-sensitive and the amount of material lost seems to have a limiting value, in contrast to materials like Epon 934 or 914 which apparently lose weight indefinitely.

Effect of Sample Thickness on Outgassing Characteristics

Because of the differences in the viscosities of the various epoxide adhesives the thickness of the final bonding layer may vary. Therefore, a correlation between the thickness of an adhesive layer and its thermal vacuum characteristics is of interest. To determine this effect, the weight loss characteristics of four samples of Epon 914 which differed only in the thickness of the adhesive layer on the aluminum strip were measured (Figs. 8 and 10). The percent loss decreases as the thickness is increased; this would be expected, because the thicker the sample, the slower the over-all diffusion rate of material to the surface. In plotting weight loss per unit area the effect is reversed; i.e., in the thicker samples more material is available for outgassing and the actual weight loss increases. It is interesting to note that within the range of experimental error, there is no change in the loss rate, in contrast to the large effect of thickness on weight loss rate noted by Gloria, et al.[3] This indicates that in the case of

[3] H. R. Gloria, W. James Stewart, and Raymond C. Savin, "Initial Weight Loss of Plastics in a Vacuum at Temperatures from 80° to 500°F" NASA Tech Note D-1329.

Epon 914 at 150°C all the volatile materials outgassing are very mobile species such as gases and low boiling solvents.

Figure 11 is a log-log plot of weight loss in g/cm^2 vs. thickness for Epon 914 after 47 hours of thermal-vacuum treatment. After this time the samples have reached a steady state, and only a relatively small amount of the total weight loss occurs. A good straight line relationship is obtained. Similarly, percent loss versus thickness (Fig. 9) gives a straight line correlation, though with a negative rather than a positive slope.

With thicknesses ranging from 0.3 to 4.0 mils, which represents an extremely useful "working interval," an accurate linear approximation may be made. This is shown in Fig. 12. This line has been drawn by the least squares method and has a root mean square (rms) deviation of only $\pm$ 0.06 x 10^{-4} g/cm^2 or approximately 5%. This allows rapid interpolation in the most useful thickness range.

It is clear that the effect of thickness on initial weight loss is very large; the initial weight loss of a sample of 3.8 mils is four to five times as great as that of a sample of 0.3 mil. However, these tests were conducted only on a single adhesive, Epon 914, and at a single temperature 150°C. Although it is reasonable to assume that thickness-weight relationships for other types of epoxy would be of the same form, the exact relationships may be determined only by direct experiment.

Effect of Amine Purity on Weight Losses

The purity of the epoxy resin has been of major concern in most industrial specifications. However, little attention has been paid to the effect of the purity of the amine curing agent on the properties of the epoxide resin. In many instances, it has been observed by us that amine curing agents oxidize and possibly absorb carbon dioxide on storage. Therefore, it was of interest to determine the effect of amine purity on the outgassing characteristics of epoxide resins. To accomplish this, a series of modified resin samples were prepared utilizing the possible combinations of pure and impure curing agent and base epoxy resin. The

outgassing characteristics of these samples were then determined (Fig. 13, Table VII).

The rather similar data for the initial weight losses reflect primarily the surface effects. The weight loss rate and weight loss at 100 hours reflect the outgassing character of the bulk of the material. It is interesting to note the dramatic effect caused by the purity of the amine, considering that it is present in relatively small amounts ($\approx$ 15%). Therefore, it is important to specify its purity.

CONCLUSIONS

On the basis of the data presented in this report, i.e., outgassing characteristics, volatiles, etc., the Epon* adhesives tested were classified according to their thermal vacuum performance. Epons 934, 931, 924, and 914 were classified as poor because they undergo thermal decomposition between 150° and 200°C. Therefore, if use temperatures exceed 150°C, other materials should be used. Epons 941 and 903 are borderline materials, i.e., they degrade slightly at temperatures near 200°C, but should be quite stable at 150°. Epons 917 and 901-B3 have very good outgassing characteristics even at 200°C, and are excellent adhesives for space craft use. This is also the case with Epon 422J if it is first postcured at 177°C to ensure complete cure and removal of the volatiles involved in the cure mechanism.

It has also been found that two factors are of considerable importance in determining the outgassing characteristics of these materials. The first factor is thickness. It has been found that an increase in thickness from approximately 0.4 to 4.0 mils, result in a fourfold increase in percent weight loss. The second factor important in outgassing characteristics is material purity. It was found that although the weight loss of the resin is fairly insensitive to the purity of the resin base, an impure curing agent greatly affects the magnitude of the weight loss parameters.

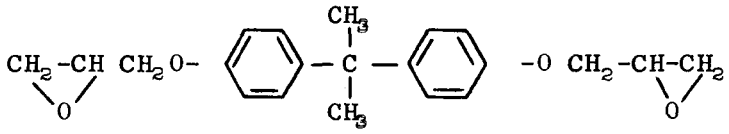
ACKNOWLEDGMENT

We wish to acknowledge the technical assistance of Mrs. Marijane Hoover.

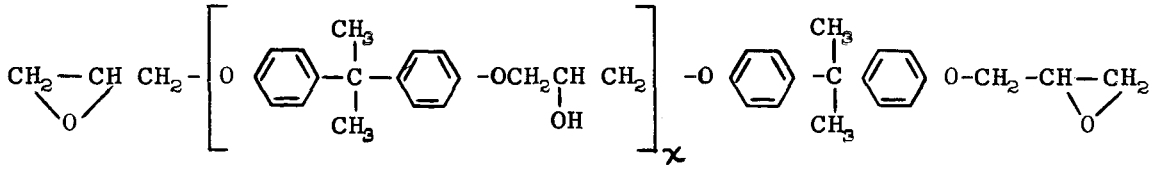
APPENDIX

CHEMISTRY OF EPOXY RESINS

The Shell Epon* adhesives are proprietary materials intended for engineering uses; the chemical compositions of these adhesives are not well known. In general, they consist of three components; an epoxy base, a "hardener" or curing agent, and a filler. Of these, only the first two are chemically active. Using IR spectroscopy the epoxy base of several of the adhesives tested has been found to be identical to Epon 828, which is based on the diglycidyl ether of Bisphenol A; its structure is



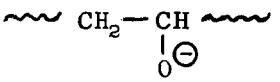
The commercial resin consists of low average molecular weight condensation products of the general structure



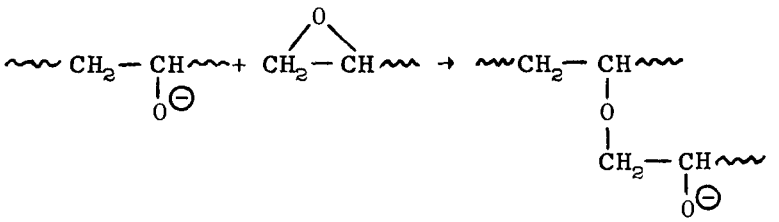
The linear polymer is cured, i.e., converted to the crosslinked resin, by use of a "hardener" or curing agent, which may be any compound having a basic group or reactive hydrogen.

Ethylene diamine and the higher polyethylene polyamines are often used as curing agents, as well as aliphatic amine salts of fatty acids which are indefinitely stable in the presence of the epoxy at room temperature, but cure rapidly when warmed. Other common curing agents are acid anhydrides, such as succinic, maleic, phthalic, and pyromellitic anhydrides.

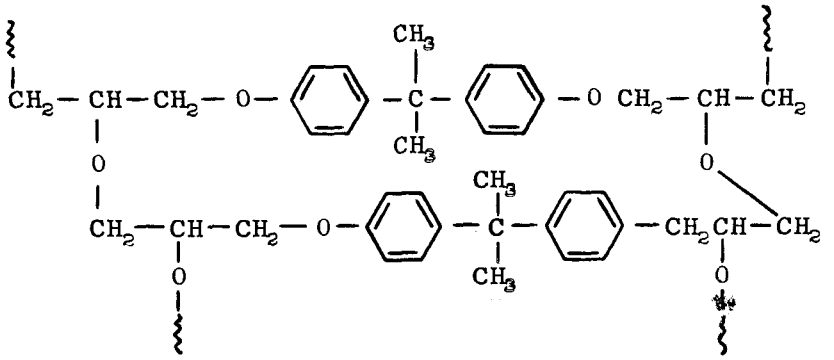
The mechanisms involved in the curing of epoxy resins are somewhat complex, but fall into two general categories. The first gives the formation of a homopolymer, where the curing agent (a base, often a tertiary amine) functions solely as a catalyst for the opening of the epoxide ring to give the species



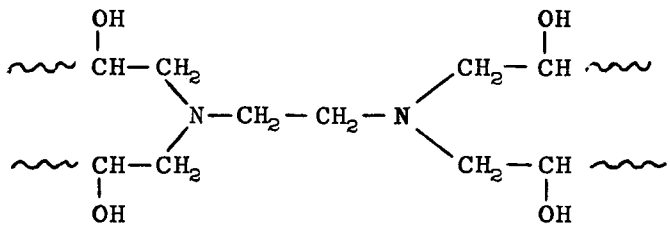
which in turn is capable of opening another epoxide ring



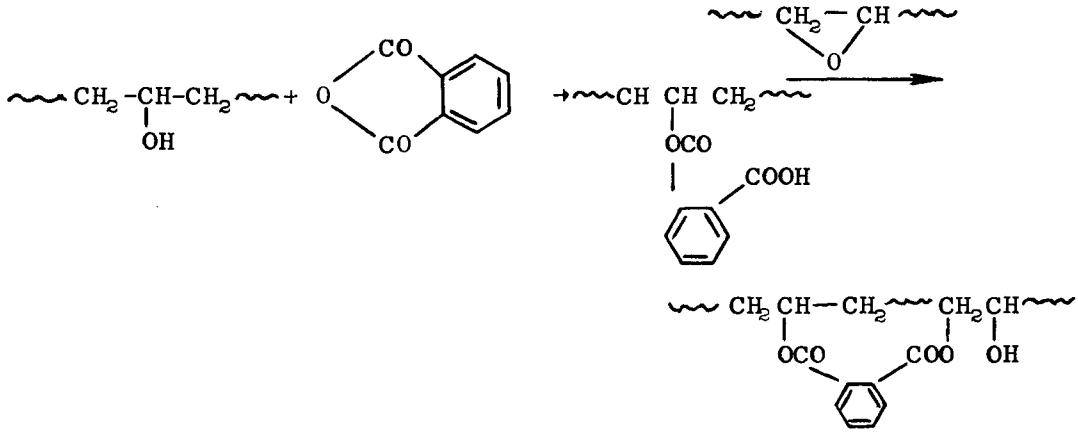
The reaction may then proceed to form an infinite, three-dimensional network of the form



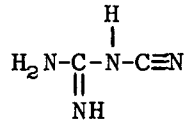
The second type of crosslinking reaction involves the incorporation of the curing agent into the epoxy network. The principal reactive cross-linking agents are dibasic acids or their anhydrides, or polyfunctional primary or secondary amines or amides. The simplest examples of this type of curing reaction is that with ethylene diamine. Each active hydrogen may react with an epoxy group, so that the final structure has the form



Dibasic acids react similarly to the amines, but the dibasic acid anhydrides have no active hydrogen and must attack first through a hydroxyl group. An example is the reaction with phthalic anhydride:



Dicyandiamide is a particularly important curing agent, (it is employed in Epons 422 and 914) having the structure



Its action is purely catalytic, i.e., it is not incorporated into the epoxy network. The mechanism of reaction is not well understood, but it is believed that catalysis is due to heat decomposition products of the dicyandiamide.

The discussion above is intended only as a general description of the types of epoxy curing reactions. In the case of the commercial resins used here, the structure of the curing agent is not generally known. Epons 901B-3 and 931 utilize an aromatic amine; 914 and 934 are cured with polyamides. Epon 917 is anhydride cured; Epon 422 is a mixed epoxy phenolic resin; no information on the curing of Epon 903 is available.

In addition it must be pointed out that the Bisphenol A based epoxy (Epon 828) is not the only resin base used. Epons 934 and 931 are novel epoxide system based on diols other than Bisphenol A.

Fillers are classed as metallic or non-metallic; the former is generally aluminum, the latter may be alumina or silica or asbestos powder.

Supplementary Data on Several Epoxide Adhesives:* Supplementary data for the development of specifications were obtained on the following adhesives: Epon 901B-3, Epon 422J (after a six hour postcure at 177°C), and Epon 917. Sample preparations followed those given in the main text of this report (see "Experimental") except that the Epon 917 test specimen was cured for two hours at 177°C rather than for one hour at 149°C. Test specimen dimensions and outgassing characteristics are tabulated below.

DIMENSIONS OF TEST SPECIMENS

Epon Resin	Cured Adhesive Weight g	Surface Area cm^2	Sample Thickness g cm^2
901B-3	0.73515	22.6	0.0325
422J	0.93751	23.2	0.0404
917	0.98435	20.2	0.0480

OUTGASSING CHARACTERISTICS

(150°C and 3 x 10^{-6} mm Hg)

Epon Resin	Initial Weight Loss		Weight Loss Rate	
	percent	g cm^{-2} x 10^4	percent/100 hr	g cm^{-2} hr^{-1} 10^4
901B-3	0.794	2.58	0.01	0.03
422J	0.946	3.83	0.10	0.40
917	0.804	3.86	0.13	0.62

All these materials reached steady state in less than 24 hours.

*This data was obtained after work was well underway on the Epoxide Adhesives report and added shortly before the report was completed.

STANFORD RESEARCH INSTITUTE

MENLO PARK
CALIFORNIA

Regional Offices and Laboratories

Southern California Laboratories
820 Mission Street
South Pasadena, California 91031

Washington Office
808–17th Street, N.W.
Washington, D.C. 20006

New York Office
270 Park Avenue, Room 1770
New York. New York 10017

Detroit Office
1025 East Maple Road
Birmingham, Michigan 48011

European Office
Pelikanstrasse 37
Zurich 1, Switzerland

Japan Office
Nomura Security Building, 6th Floor
1–1 Nihonbashidori, Chuo-ku
Tokyo, Japan

Retained Representatives

Toronto, Ontario, Canada
Cyril A. Ing
67 Yonge Street, Room 710
Toronto 1, Ontario, Canada

Milan, Italy
Lorenzo Franceschini
Via Macedonio Melloni, 49
Milan, Italy